



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/01394 <b>(22) International Filing Date:</b> 21 February 1992 (21.02.92)  <b>(30) Priority data:</b> 674,007 25 March 1991 (25.03.91) US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/ US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).  <b>(72) Inventor:</b> MALONE, Bruce, A. ; 3130 Granview Drive, Granville, OH 43023 (US).  <b>(74) Agent:</b> DEAN, J., Robert, Jr.; The Dow Chemical Com- pany, P.O. Box 515, Granville, OH 43023-0515 (US).		<b>(81) Designated States:</b> AT (European patent), AU, BE (Euro- pean patent), BR, CA, CH (European patent), DE (Eu- ropean patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European pa- tent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> NONDISTORTED POLYOLEFIN FOAM STRUCTURES AND PROCESS FOR MAKING  <b>(57) Abstract</b>  Disclosed is a closed-cell, non-crosslinked foam structure of a ratio of minor dimension to major dimension of 1/8 or less comprising a plurality of coalesced extruded strands or profiles of a foamed polyolefin composition having an average cell size of from 0.02 to 0.5 millimeters. The cross-sectional geometry of the foam structure substantially corresponds to the overall arrangement of the orifices of the die from which the foamed polyolefin composition was extruded. Further disclosed is a process for making the above foam structure comprising extruding a foamable polyolefin composition through the multiorifice die to form the structure.		

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-1-

NONDISTORTED POLYOLEFIN FOAM STRUCTURES  
AND PROCESS FOR MAKING

Background of the Invention

5       The invention relates to a closed-cell, non-crosslinked polyolefin foam structure of relatively small cell size and relatively low cross-section minor to major dimension ratio. The extruded structure is substantially free of distortion, convolution, or corrugation from its intended shape or geometry.

10       Solid closed-cell polyolefin foam structures of relatively low cross-section minor to major dimension ratio, height to width in the case of those of rectangular cross-section, have found numerous commercial applications such as cushioning, packaging,  
15       insulation, sheeting, and the like. To enhance insulative performance, softness, sound absorption, and nonabrasiveness of such structures, it would be desirable to reduce the cell size of the polyolefin foam  
20       comprising the structure.

      A problem with making solid closed-cell, non-crosslinked polyolefin foam structures of relatively small cell sizes (e.g. 0.02 to 0.5 millimeters (mm)) and  
25       relatively low cross-section dimension ratios ( .g. 1/8

-2-

or less) is that the structure actually formed may be in a geometry or shape other than that intended. As the foamable composition from which the structure is made exits the die, it is not able to expand directionally outward with respect to the major dimension of the die orifice at a rate sufficient to prevent the structure from becoming distorted, convoluted, or corrugated along its major dimension. The structure cannot expand rapidly enough because relatively small cell size foams have relatively high foaming rates, which result from the relatively high levels of nucleator required to make foams having relatively small cell size.

It would be desirable to have a closed-cell, non-crosslinked polyolefin foam structure of relatively low cross-section minor to major dimension ratio comprised of a polyolefin foam of relatively small cell size. Such foam structure would be substantially free of deviation or distortion from its intended shape or geometry.

#### Summary of the Invention

According to the present invention, there is a closed-cell, non-crosslinked foam structure of a ratio of minor dimension to major dimension of about 1/8 or less in cross-section comprised of coalesced strands or profiles of a foamed polyolefin composition having an average cell size of from 0.02 to 0.5 millimeters. The foam structure substantially corresponds in cross-sectional geometry to the geometry of the overall arrangement of the orifices of the die from which it was extruded. The extrusion of the foam structure in the form of coalesced strands or profiles allows structures of such relative cross-sectional dimension ratios (e.g.

-3-

height to width for rectangular structures) in such a size range to be formed without distortion, convolution, or corrugation from the intended or desired shape or geometry. Distortion, convolution, or corrugation from the intended or desired shape or geometry is  
5 substantially avoided because the strands or profiles expand into the channels between themselves instead of foam expanding against itself as in a solid foam.

10 According to the present invention, there is a process for making a closed-cell, non-crosslinked foam structure of a ratio of minor dimension to major dimension in cross-section of  $1/8$  or less and comprised of a foamed polyolefin composition having an average  
15 cell size of from 0.02 to 0.5 millimeters. The process comprises extruding a foamable polyolefin composition through a die defining a plurality of orifices therein to form a plurality of coalesced extruded strands or profiles of the foamed polyolefin composition forming  
20 the above foam structure substantially corresponding to the geometry of the overall arrangement of the orifices of the die.

#### Detailed Description

25 The present foam structure is formed of coalesced closed-cell, non-crosslinked polyolefin foam strands or profiles having an average cell size of from 0.02 to 0.5 millimeters and minor to major dimension  
30 ratios of less than  $1/8$  or less to be made substantially corresponding to the shape or geometry of the overall arrangement of the orifices of the die from which the structure was extruded. The present foam structure circumvents the problems associated with prior art foam structures of that cell size range and relative

-4-

dimension by its ability to accommodate the high rate of foaming without being distorted, convoluted, or corrugated.

5       The present foam structure is formed by  
extrusion of a molten foamable, non-crosslinked  
polyolefin composition through a multiorifice die. The  
foamable composition is formed by melt plastifying the  
polyolefin and blending therein a blowing agent and  
other additives such as a nucleating agent. The  
10       orifices of the multiorifice die are arranged so that  
contact between adjacent streams of the molten extrudate  
occurs during the foaming process and the contacting  
surfaces adhere to one another with sufficient adhesion  
to result in a unitary foam structure. The streams of  
15       molten extrudate exiting the die take the form of  
strands or profiles, which desirably foam, coalesce, and  
adhere to one another to form a unitary structure.  
Desirably, the coalesced individual strands or profiles  
20       of polyolefin foam should remain adhered into unitary  
structure to prevent strand delamination under stresses  
encountered in preparing, shaping, and using the foam.  
Apparatuses and methods for producing foam structures of  
strand form are seen in U.S. Patents 3,573,152 and  
25       4,824, 720.

30       The strands or profiles will vary in cross-  
sectional shape or geometry according to the shape or  
geometry of the orifices in the die. The strands or  
profiles may be the same or different shape or geometry  
than the foam structure which they coalesce to form.  
The orifices may take on a circular shape or a  
noncircular shape though circular is preferred.  
Suitable noncircular shapes include X-shaped, cross- or

-5-

star-shaped, or polygonal-shaped. The various orifices in the die may be specially arranged in a desired configuration or array such as a sine wave, honeycomb, square saw tooth, or a triangular saw tooth wave pattern. Preferably, the individual strands, have a major dimension in cross-section, diameter in the case of circular strands, of between 0.5 and 10 millimeters and most preferably between 1.0 and 5.0 millimeters.

The orifices in the die will be of shape or geometry and be specially arranged such that there will be sufficient channel volume or clearance between the streams of molten extrudate exiting from the same for them to foam to form the strands or profiles without substantial distortion, convolution, or corrugation of the resulting unitary foam structure relative to the geometry of the overall arrangement of the orifices. The streams of molten extrudate may foam to either partly or completely fill the open channel volume between the strands or profiles.

The geometry or shape of the resulting foam structure will substantially correspond to the overall arrangement or geometry of the die orifices or, in other words, to the intended or desired shape or geometry. For instance, a plurality or multiplicity of circular orifices arranged in a rectangular pattern will yield a rectangular foam structure. A plurality or multiplicity of circular orifices arranged in a circular pattern will yield a cylindrical or circular foam structure. The geometry or shape of the present foam structure will correspond to the overall arrangement or geometry of the orifices in the die from which it is extruded without

-6-

substantial distortion, convolution, or corrugation therefrom.

5       The foam structure typically will have cross-sectional dimensions larger than the dimensions defined by the overall arrangement or geometry the die orifices of the die from which it was extruded due to foaming of the molten extrudate, but the relative cross-sectional dimensions of the foam structure will substantially correspond to the relative dimensions of the overall arrangement or geometry of the die orifices. For instance, in the case of a rectangular arrangement of circular die orifices, the resulting foam structure will have rectangular cross-sectional dimensions exceeding that of the overall arrangement or geometry of the die orifices, but will have substantially the same relative cross-sectional dimensions.

20       Blending of various components in the method of the present invention in order to provide suitable foamable polyolefin compositions accomplished according to known techniques in the art. Suitably, a mixer, extruder, or other suitable blending device is employed to obtain a homogeneous melt. The extruder or other suitable blending device is also employed to incorporate a blowing agent. Nucleating agents, extrusion aids, antioxidants, colorants, pigments, etc. may also be incorporated as desired.

30       Suitable foamable polyolefin compositions include polyethylene or polypropylene. Preferred are copolymers of ethylene and a monoethylenically unsaturated polar monomer copolymerizable therewith, specially carboxyl-containing comonomers. Examples include copolymers of ethylene and acrylic acid or

-7-

methacrylic acid and C<sub>1-4</sub> alkyl ester or ionomeric derivatives thereof; ethylene vinyl-acetate copolymers; ethylene/carbon monoxide copolymers; anhydride containing olefin copolymers of a diene and a polymerizable; copolymers of ethylene and an  $\alpha$ -olefin having ultra low molecular weight (i.e., densities less than 0.92 grams/cubic centimeter); blends of all of the foregoing resins; blends thereof with polyethylene (high, intermediate or low density); etc. Particularly preferred compositions are copolymers of ethylene and acrylic acid, (EAA copolymers) having up to about 30 percent by weight of copolymerized acrylic acid; ionomeric derivatives of the foregoing, copolymers of ethylene and vinyl acetate; ultra low density polyethylene; and blends of the foregoing with one another and with low density polyethylene.

The polymers of ethylene and a polar comonomer may be prepared by known addition polymerization techniques, or by a grafting reaction of the reactive comonomer with a preformed polymer of ethylene. Additional elastomeric components such as polyisobutylene, polybutadiene, ethylene/propylene copolymers, and ethylene/propylene diene interpolymers may be included in the blend if desired.

A most preferred resin composition comprises a copolymer of ethylene and acrylic acid or ethylene and vinyl acetate containing from 85 percent to 98 percent ethylene by weight. A most preferred polyolefin composition comprises a homogeneous, random copolymer of ethylene and acrylic acid. Copolymers of ethylene and acrylic acid or of ethylene and vinyl acetate may be obtained from The Dow Chemical Company. Ethylene vinyl acetate copolymer may also be obtained under tradename

-8-

Elvax from E. I. duPont de Nemours & Company. Anhydrid modified copolymers or ethylene are available under the tradename Plexar from Norchem, Inc. Ionomeric copolymers are available under the tradename Surlyn from E. I. duPont de Nemours & Company.

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The polyolefin composition comprises greater than 50 percent, preferably greater than 80 percent, and more preferably greater than 95 percent polyolefin by weight of the foam structure.

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The present foam structure is extruded with one or more of any blowing agents known in the art. Suitable blowing agents include halocarbons such as fluorocarbons and chlorofluorocarbons; hydrohalocarbons such as hydrofluorocarbons and hydrochlorofluorocarbons; alkylhalides such as methyl chloride and ethyl chloride; hydrocarbons such as the alkanes or alkenes of 2 to 9 carbon atoms; common gases such as air, carbon dioxide, nitrogen, argon; water; or mixtures of any of the above.

20

Preferred blowing agents are alkanes such as butane, isobutane, pentane, isopentane, hexane, isohexane, heptane, and the like. A most preferred blowing agent is isobutane. hydrocarbons such as alkanes are preferred due to their relatively low ozone depletion potential. Suitable blowing agents also include chemical blowing agents such as ammonium and azo type compounds. Such compounds include ammonium carbonate, ammonium bicarbonate, potassium bicarbonate, diazoaminobenzene, diazoaminotoluene, azodicarbonamide, diazoisobutyronitrile, and the like.

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The term non-crosslinked foam structure means that the foam composition comprising the strands from

-9-

which the foam structure is formed is substantially free of crosslinking. The term non-crosslinked is inclusive however, of the slight degree of crosslinking which may occur naturally without the use of crosslinking agents.

5           Suitable foam structures have gross densities (that is bulk densities or densities of the closed-cell foam including interstitial channels or voids between strands or profiles), preferably varying from 3.2 to 48 kilograms per cubic meter ( $\text{kg/m}^3$ ). Most preferred foam  
10 structures have a density from 8.0 to 45  $\text{kg/m}^3$ . For specific uses in low weight cushioning applications a preferable alternate embodiment comprises portions having densities less than 32  $\text{kg/m}^3$ . The individual  
15 strands of foam comprising the foam structure preferably possess a local or strand density from 8.0 to 96  $\text{kg/m}^3$ , and most preferably from 16 to 48  $\text{kg/m}^3$ .

20           The present foam structure is comprised of foam strands having an average cell size of between 0.02 to 0.5 millimeters. A particularly preferred foam structure is comprised of foam strands having an average cell size of between 0.1 and 0.3 millimeters.

25           In the present closed-cell foam structure, preferably at least 70 percent closed-cell according to ASTM D-2856 not including interstitial channels or voids between the foam strands comprising the foam structure.

30           To further illustrate the present invention, a nonlimiting example of same is provided below.

#### EXAMPLE

A polyolefin foam structure of the present invention was formed by extruding a composition of

-10-

p lyethylene/ Surlyn® 8660 ionom r in a 90/10 w ight  
ratio, 26 parts per hundred CFC-114/CFC-12 in a 80/20  
weight ratio, and 0.8 parts per hundred at a rate of 136  
kilograms per hour through a multiorifice die containing  
5 1500 circular orifices arranged in a rectangular  
configuration. The resulting structure had a cross-  
sectional dimension of 3.8 centimeters by 62.2  
centimeters and an average cell size of 0.3 millimeters.  
The structure was substantially free of distortion,  
10 convolution, or corrugation from its intended  
rectangular shape.

While embodiments of the method and the foam of  
the present invention have been shown with regard to  
15 specific details, it will be appreciated that depending  
upon the manufacturing process and the manufacturer's  
desires, the present invention may be modified by  
various changes while still being fairly within the  
scope of the novel teachings and principles herein set  
20 forth.

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-11-

## WHAT IS CLAIMED IS:

1. A process for making a closed-cell, non-crosslinked, nondistorted extruded foam structure of a ratio of minor dimension to major dimension in cross-section of about  $1/8$  or less and comprised of a foamed polyolefin composition having an average cell size of from 0.02 to 0.5 millimeters, comprising: a) forming a foamable polyolefin composition capable of forming a foamed polyolefin composition having an average cell size of from 0.02 to 0.5 millimeters, b) extruding the foamable composition through a die defining a plurality of orifices therein having an overall arrangement of minor to major dimension in cross-section of  $1/8$  or less to form a plurality of foamable strands and c) allowing the foamable strands to expand and coalesce to form the foam structure.

2. The process of Claim 1, wherein the foam structure is generally rectangular in cross-section.

3. The process of Claim 1, wherein the polyolefin comprises polyethylene or a copolymer thereof.

-12-

4. The process of Claim 1, wherein the polyolefin comprises polypropylene or a copolymer thereof.

5 5. The process of Claim 1, wherein the foamed polyolefin composition has an average cell size of between 0.1 and 0.3 millimeters.

6. A foam structure made according to the process of Claim 1.

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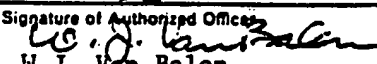
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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01394

<b>I. CLASSIFICATION &amp; SUBJECT MATTER</b> (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): B32B 3/26 U.S. CL. 428/71, 314.4, 314.8, 316.6		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched ?		
Classification System	Classification Symbols	
U.S.	428/71, 314.4, 314.8, 316.6	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
Y	US, A, 3,949,031 (FAIRBANKS) 06 APRIL 1976. See entire document.	1-6
Y	US, A, 4,753,841 (NOEL) 28 JUNE 1988. See entire document.	1-6
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: **</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
19 MAY 1992	04 JUN 1992	
International Searching Authority	Signature of Authorized Officer	
ISA/US	 W.J. Van Balen	